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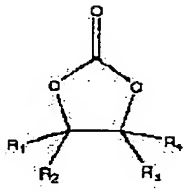
(54) NONAQUEOUS ELECTROLYTE FOR SECONDARY BATTERY AND NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a secondary battery nonaqueous electrode which is fire- resistant and superior in charging and discharging characteristic, and a nonaqueous electrolyte secondary battery capable of safely generating a high voltage and excellent in charging and discharging characteristic obtained by use of such a nonaqueous electrolyte.
SOLUTION: This nonaqueous electrolyte is formed of a nonaqueous solvent containing a cyclic carbonic ester, represented by the formula and a phosphoric ester compound, and an electrolyte. In the formula, R1-R4, which may be the same or different with respect to each other, represent hydrogen atom, a 1-7C alkyl group, a 2-7C hydrogen carbonate group containing non-conjugate unsaturated bonds, -CH2OR5 or -CH2OCOR6 (R5, R6 represent a 1-7C alkyl group or a 2-7C hydrogen carbonate containing non-conjugate unsaturated bonds), and at least of R1-R4 is the group containing non-conjugate unsaturated bonds.



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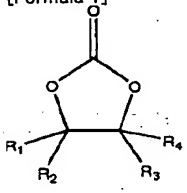
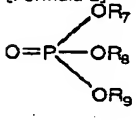
CLAIMS

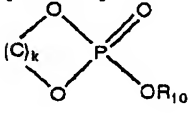
[Claim(s)]
[Claim 1] Nonaqueous electrolyte for rechargeable batteries characterized by the bird clapper from the non-aqueous solvent containing the annular carbonate expressed with the following general formula [I], and a phosphoric ester compound, and an electrolyte.
[Formula 1]



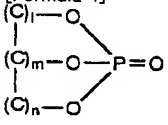
[I]
(Among the formula [I], even if R1-R4 are mutually the same, you may differ.) The carbon atomic number in which a hydrogen atom and a carbon atomic number include the alkyl group of 1-7 and a disconjugation system unsaturated bond The hydrocarbon group of 2-7, - it is CH2OR5 or -CH2OCOR6, and is the basis in which at least one of R1-R4 includes a disconjugation system unsaturated bond
[Claim 2] Nonaqueous electrolyte for rechargeable batteries according to claim 1 characterized by the carbon atomic number to which the annular carbonate expressed with the above-mentioned general formula [I] includes a disconjugation system unsaturated bond in at least one of R1-R4 having the hydrocarbon group of 2-7.
[Claim 3] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to which the annular carbonate expressed with the above-mentioned general formula [I] is characterized by being what has -CH2OR5 or -CH2OCOR6 (the carbon atomic number in which R5 and R6 include a disconjugation system unsaturated bond shows the hydrocarbon group of 2-7.) in at least one of R1-R4.
[Claim 4] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to 3 to which a carbon atomic number including the aforementioned disconjugation system unsaturated bond is characterized by the hydrocarbon group of 2-7 being an alkenyl machine.
[Claim 5] Nonaqueous electrolyte for rechargeable batteries according to claim 1 characterized by the aforementioned phosphoric ester compound being phosphoric ester expressed with following general formula [II] - [IV].
[Formula 2]



[II]
[Formula 3]



[III]
[Formula 4]



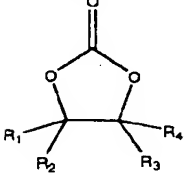
[IV]
(Among a formula, even if R7-R10 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers.

[Claim 6] Nonaqueous electrolyte for rechargeable batteries according to claim 5 to which the aforementioned phosphoric ester compound is characterized by being trimethyl phosphate.
[Claim 7] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to 6 characterized by the aforementioned non-aqueous solvent containing further at least one sort of carbonates chosen from the annular carbonates and chain-like carbonates other than the above [I].
[Claim 8] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to 7 characterized by an electrolyte being lithium salt.
[Claim 9] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to 8 characterized by the nonaqueous electrolyte for rechargeable batteries being the electrolytic solution for rechargeable lithium-ion batteries.
[Claim 10] The nonaqueous electrolyte rechargeable battery characterized by the negative electrode which contains a metal lithium, a lithium content alloy, or the carbon material in which the dope and ** dope of a lithium ion are possible as a negative-electrode active material, the positive electrode which contains either a lithium, the multiple oxides of transition metals and carbon materials or such mixture as a positive active material, and having nonaqueous electrolyte for rechargeable batteries according to claim 1 to 9 as the electrolytic solution.

[Translation done.]

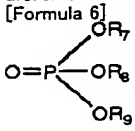
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte rechargeable battery containing this electrolytic solution while relating to the nonaqueous electrolyte for rechargeable batteries which it is still more detailed, and fire retardancy is high, was safe, and could generate the high voltage, and was excellent in the cell charge-and-discharge property about the nonaqueous electrolyte for rechargeable batteries, and a nonaqueous electrolyte rechargeable battery.
[0002]
Background of the Invention] Nonaqueous electrolyte is used as the electrolytic solution of energy-storage devices, such as a lithium cell, and since these devices have a high voltage and high-energy density and are excellent in reliability, they are widely used for the power supply of consumer electronics etc. Nonaqueous electrolyte consists of a non-aqueous solvent and an electrolyte, and propylene carbonate [which is generally the organic solvent of a high dielectric constant], gamma-butyrolactone, sulfolane or dimethyl carbonate [that is the organic solvent of hypoviscosity], dimethoxyethane, tetrahydrofuran, 1, and 3-dioxolane etc. is used as a non-aqueous solvent. Moreover, as an electrolyte, Et4NBF4, LiBF4, LiPF6, LiClO4 and LiAsF6, LiCF3SO3, LiAlCl4, LiSiF6, etc. are used.
[0003] By the way, since a cell with a high energy density is desired, research is advanced about the high-voltage cell. For example, the rechargeable battery called rocking-chair type which used the lithium of LiCoO2, LiNiO2, and LiMn2O4 grade and the multiple oxide of transition metals for the positive electrode of a cell, and used the carbon material for the negative electrode is studied. since [in this case,] a cell voltage can generate more than 4V and moreover does not have a deposit of a metal lithium -- overcharge and external short-circuit -- ****(ing) -- crushing -- etc. -- also by experiment, it is checked that safety is secured and it appears on the market as a noncommercial use However, when the future large formation of high-energy density and enlargement are made, to raise safety further is desired and it is called for that inflammable nonaqueous electrolyte has self-extinguishing. For this reason, adding the phosphoric ester known as a compound with self-extinguishing to the electrolytic solution is proposed (for example, refer to JP,4-184870,A).
[0004] However, although the electrolytic solution which added general phosphoric ester, such as phosphoric-acid triethyl, is fire retardancy and safety improved, depending on the kind and addition of phosphoric ester, there were also cell charge-and-discharge efficiency, an energy density of a cell, and a thing that cannot necessarily be satisfied in respect of a battery life. Although limiting the addition of phosphoric ester (for example, referring to JP,7-114940,A) etc. was proposed in order to solve such a problem for example, it was not what is not necessarily satisfied in respect of fire retardancy, safety, cell charge-and-discharge efficiency, the energy density of a cell, a battery life, etc.
[0005]
[Objects of the Invention] this invention aims at offering the rechargeable battery containing this nonaqueous electrolyte while it aims at offering the nonaqueous electrolyte for rechargeable batteries which was made in view of the above-mentioned trouble, fire retardancy was highly safe, and could generate the high voltage, and was excellent in cell charge/discharge capability ability.
[0006]
[Summary of the Invention] The nonaqueous electrolyte for rechargeable batteries concerning this invention is characterized by the bird clapper from the non-aqueous solvent containing the annular carbonate expressed with the following general formula [I], and a phosphoric ester compound, and the electrolyte.
[0007]
[Formula 5]

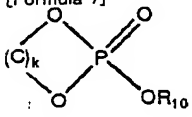


[I]
Among the formula [I], even if R1-R4 are mutually the same, you may differ. The carbon atomic number in which a hydrogen atom and a carbon atomic number include the alkyl group of 1-7 and a disconjugation system unsaturated bond The hydrocarbon group of 2-7, - It is CH2OR5 or -CH2OCOR6, and at least one of R1-R4 is a basis including a disconjugation system unsaturated bond.
[0008] That in which the carbon atomic number which includes a disconjugation system unsaturated bond in at least one of the annular carbonate expressed with the above-mentioned general formula [I], and R1-R4 has the hydrocarbon group of 2-7 is desirable, and it is desirable that it is an ARUKENIRU machine especially. moreover, among [the cyclic ester expressed with the above-mentioned general formula [I], and among R1-R4] -- at least one -CH2OR5 or -CH2OCOR6 -- it is (the carbon atomic number in which, as for R5 and R6, a carbon atomic number

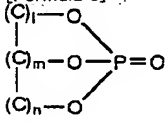
includes the alkyl group or disconjugation system unsaturated bond of 1-7 shows the hydrocarbon group of 2-7) — what it has is desirable
[0009] It is desirable that it is phosphoric ester expressed with following general formula [II] - [IV], and the aforementioned phosphoric ester compound is [0010].
[Formula 6]



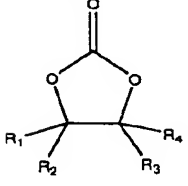
[II]
[0011]
[Formula 7]



[III]
[0012]
[Formula 8]

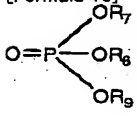


[IV]
(Among a formula, even if R7-R10 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers. It is desirable especially that it is trimethyl phosphate. The thing of an annular carbonate and a chain-like carbonate for which the aforementioned non-aqueous solvent includes 1. kind at least is still more desirable. As for an electrolyte, it is desirable that it is lithium salt.
[0013] The nonaqueous electrolyte rechargeable battery concerning this invention is characterized by the negative electrode which contains a metal lithium, a lithium content alloy, or the carbon material in which the dope and ** doping of a lithium ion are possible as a negative-electrode active material, the positive electrode which contains either a lithium, the multiple oxides of transition metals and carbon materials or such mixture as a positive active material, and including the aforementioned nonaqueous electrolyte for rechargeable batteries as the electrolytic solution.
[0014]
[Detailed Description of the Invention] Hereafter, the nonaqueous electrolyte concerning this invention and the nonaqueous electrolyte rechargeable battery using this nonaqueous electrolyte are explained concretely. The nonaqueous electrolyte for rechargeable batteries concerning this invention consists of a non-aqueous solvent containing a specific annular carbonate and a specific phosphoric ester compound, and an electrolyte.
[0015] What is expressed with the following general formula [I] as an annular carbonate used by the annular carbonate this invention is used.
[0016]
[Formula 9]

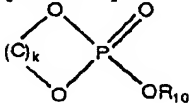


[I]
Among the formula [I], even if R1-R4 are mutually the same, you may differ. The carbon atomic number in which a hydrogen atom and a carbon atomic number include the alkyl group of 1-7 and a disconjugation system unsaturated bond The hydrocarbon group of 2-7, - It is CH2OR5 or -CH2OCOR6 (the carbon atomic number in which, as for R5 and R6, a carbon atomic number includes the alkyl group or disconjugation system unsaturated bond of 1-7 shows the hydrocarbon group of 2-7), and is the basis in which at least one of R1-R4 includes a disconjugation system unsaturated bond.
[0017] What the carbon atomic number in which at least one of R1-R4 includes a disconjugation system unsaturated bond has the hydrocarbon group of 2-7, and has -CH2OR5 or -CH2OCOR6 (the carbon atomic number in which R5 and R6 include a disconjugation system unsaturated bond shows the hydrocarbon group of 2-7) is desirable as cyclic ester expressed with such an above-mentioned general formula [I] by this invention. It is desirable that a carbon

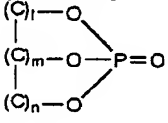
atomic number including such a disconjugation system unsaturated bond is an ARUKENIRU machine as a hydrocarbon group of 2-7.
[0018] As an annular carbonate expressed with such a formula [I] 4-vinyl ethylene carbonate, 4, and 4-divinyl ethylene carbonate, Vinyl ethylene carbonate derivative;4-vinyl-4-methyl-ethylene carbonate, such as 4 and 5-divinyl ethylene carbonate, 4-vinyl-5-methyl-ethylene carbonate, the 4-vinyl -4, 5-dimethyl ethylene carbonate, The 4-vinyl -5, 5-dimethyl ethylene carbonate, 4-vinyl - Alkylation vinyl ethylene carbonate derivative;4-allyloxy methyl-ethylene carbonate, such as 4, 5, and 5-trimethylethylene carbonate, Allyloxy methyl-ethylene carbonate derivative;4-methyl-4-allyloxy methyl-ethylene carbonate, such as 4 and 5-diaryl oxymethyl ethylene carbonate, Alkylation allyloxy methyl-ethylene carbonate, such as 4-methyl-5-allyloxy methyl-ethylene carbonate; 4-acrylic oxymethyl ethylene carbonate, Acrylic oxymethyl ethylene carbonate derivative;4-methyl-4-acrylic oxymethyl ethylene carbonate, such as 4 and 5-JIAKURIRU oxymethyl ethylene carbonate, Alkylation acrylic oxymethyl ethylene carbonate, such as 4-methyl-5-acrylic oxymethyl ethylene carbonate, etc. is mentioned.
[0019] Among these, the thing containing vinyl ethylene carbonate derivatives, such as 4-vinyl ethylene carbonate, 4, and 4-divinyl ethylene carbonate, 4, and 5-divinyl ethylene carbonate, is desirable.
[0020] There is an effect of improving the charge-and-discharge efficiency of the cell produced in case a phosphoric ester compound is added, and the fall of a load characteristic in such an annular carbonate.
As a phosphoric ester compound used by the phosphoric ester compound this invention, the phosphoric ester expressed with following general formula [II] - [IV] is used preferably.
[0021]
[Formula 10]



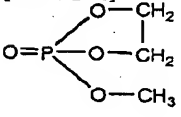
[II]
[0022]
[Formula 11]



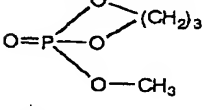
[III]
[0023]
[Formula 12]



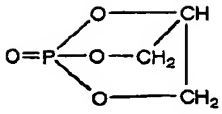
[IV]
(Among a formula, even if R7-R10 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers.
Specifically as phosphoric ester expressed with a formula [II], trimethyl phosphate, triethyl phosphate, TORIPURO pill phosphate, tributyl phosphate, dimethyl ethyl phosphate, methyl diethyl phosphate, etc. are mentioned. Specifically as phosphoric ester expressed with a formula [III], it is methyl-ethylene phosphate and [0024].
[Formula 13]



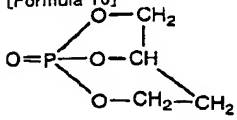
Methyl trimethylene phosphate [0025]
[Formula 14]



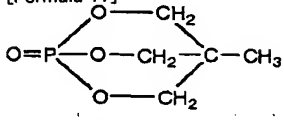
**** is mentioned. Specifically as phosphoric ester expressed with a formula [IV], it is [0026].
[Formula 15]



[0027]
[Formula 16]



[0028]
[Formula 17]



Trimethylolethane phosphate etc. is mentioned.
[0029] In respect of fire-resistant grant, since the effect is large, trimethyl phosphate and phosphoric-acid triethyl are desirable, and especially trimethyl phosphate is [among these] desirable.
[0030] In the nonaqueous electrolyte for rechargeable batteries concerning a non-aqueous-solvent this invention, the non-aqueous solvent containing the annular carbonate expressed with the above general formulas [I] and a phosphoric ester compound is used. As for the aforementioned phosphoric-acid ESUDERU compound, in the binary system of an annular carbonate and a phosphoric ester compound, it is desirable to be preferably contained in 90 - 99.9% of the weight of the amount still more preferably 80 to 99.99% of the weight 60 to 99.999% of the weight in a non-aqueous solvent. If the phosphoric ester compound is contained in the non-aqueous solvent in such an amount, sufficient fire retardancy for the nonaqueous electrolyte for rechargeable batteries can be given.
[0031] Moreover, as for the annular carbonate expressed with a general formula [I], it is desirable to be preferably added in 0.1 - 10% of the weight of the amount still more preferably 0.01 to 20% of the weight 0.001 to 40% of the weight to a non-aqueous solvent. The charge-and-discharge efficiency of the cell produced in case a phosphoric ester compound will be added, if the annular carbonate expressed with a general formula [I] in a non-aqueous solvent in such an amount is added, and the fall of a load characteristic are fully improvable.
[0032] With the non-aqueous solvent used by this invention In addition to the annular carbonate expressed with a general formula [I], and a phosphoric ester compound, it is desirable to contain carbonates, such as other annular carbonates and a chain-like carbonate. By including such a carbonate, the charge-and-discharge efficiency and the load characteristic of a cell are further improvable. As other annular carbonates, ethylene carbonate, propylene car PONETO, butylene carbonate, etc. are mentioned. these — one sort — or two or more sorts may use it, mixing The mixed solvent of ethylene carbonate, propylene carbonate or ethylene carbonate, and propylene carbonate is preferably used among these annular carbonates. If these annular carbonates are contained, it is possible to raise the solubility of the electrolyte in low temperature, transportation of an electrolyte can become easy, and the electrical conductivity of the electrolytic solution can be raised further.
[0033] As a chain-like carbonate, dimethyl carbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, ethyl propyl carbonate, etc. are mentioned. these — one sort — or two or more sorts may use it, mixing Since dimethyl carbonate can raise the self-extinguishing of the electrolytic solution among these chain-like carbonates, it is desirable.
[0034] If these chain-like carbonic acid ESUDERU is contained in the non-aqueous solvent, it is possible to make low viscosity of the nonaqueous electrolyte for rechargeable batteries, and electrolytic solubility can be raised further and it can consider as the electrolytic solution excellent in the electrical conductivity in ordinary temperature or low temperature. The above chain-like carbonates and annular carbonates can also be mixed and used.
[0035] In the case of the three-component system which mixes and uses other the above cyclic ester and chain-like carbonates for the annular carbonate and phosphoric ester compound which are expressed with a general formula [I], the annular carbonate expressed with a general formula [I] is 0.001 - 40 % of the weight usually preferably used at 0.1 - 5% of the weight of a rate still more preferably 0.01 to 20% of the weight to the non-aqueous-solvent whole quantity.

[0036] case [moreover,] it is the same — a phosphoric ester compound — the non-aqueous-solvent whole quantity — receiving — usually — 0.1 - 99.999 % of the weight — desirable — 1 - 99.99 % of the weight — further — desirable — 3 - 60 % of the weight — it comes out comparatively and is used — having — other cyclic ester and chain-like carbonates — the non-aqueous-solvent whole quantity — receiving — usually — 99.899 or less % of the weight — desirable — 98.9 or less % of the weight — further — desirable — 35 - 96.9 % of the weight — it comes out comparatively and is used
[0037] If it is possible to raise the electrical conductivity of the nonaqueous electrolyte for rechargeable batteries if other annular carbonates are contained in the non-aqueous solvent in such an amount and the chain-like carbonate is contained, the nonaqueous electrolyte for rechargeable batteries excellent in self-extinguishing can be obtained.
[0038] The annular carbonate expressed with the above-mentioned phosphoric ester and a general formula [I] to the non-aqueous solvent used by this invention further again, The methyl formate usually used as a non-aqueous solvent for cells besides other annular carbonates and a chain-like carbonate, An ethyl formate, a propyl formate, methyl acetate, ethyl acetate, propyl acetate, Chain-like ether, such as chain-like ester, such as a methyl propionate and an ethyl propionate, and dimethoxyethane, Amides, such as cyclic ether, such as a tetrahydrofuran, and a

dimethylformamide Methyl - ******-BAMETO, such as N and N-dimethyl carver mate Annular sulfones, such as cyclic ester, such as gamma-butyrolactone, and a sulfolane Non-aqueous solvents, such as annular ureas, such as cyclic-amides [, such as annular carver mates, such as N-methyl OKISASORIJINON and N-methyl pyrrolidone,], N, and N-dimethyl imidazolidone, can be used to about 40 % of the weight to the whole quantity of a non-aqueous solvent.

[0039] As an electrolyte used by the electrolyte this invention, usually, if used as an electrolyte for nonaqueous electrolyte, it can be used, without being limited especially. Specifically LiPF6, LiBF4, LiClO4, LiAsF6, LiOSO2R11, LiN (SO two R12) (SO two R13), R11-R18 among LiC (SO two R14) (SO two R15) (SO two R16) and a LiN(SO2OR17) (SO2OR18) [formula It may differ, even if mutually the same, and lithium salt, such as] and LiSiF6 which are the perfluoroalkyl machine of carbon numbers 1-6, LiC4F9SO3, and LiC3F17SO3, is used preferably. These lithium salt may be used independently, and may mix and use two or more sorts of lithium salt.

[0040] Since LiPF6 and LiBF4 become [fire retardancy] high by the synergism with phosphoric ester among these lithium salt, it is desirable. As for such an electrolyte, it is usually desirable to contain 0.1-3 mols /in the nonaqueous electrolyte for rechargeable batteries by the concentration of 0.5-2 mols/l. preferably l.

The nonaqueous electrolyte rechargeable battery concerning a nonaqueous electrolyte rechargeable battery this invention consists of a negative electrode which contains a metal lithium, a lithium content alloy, or the carbon material in which the dope and ** doping of a lithium ion are possible as a negative-electrode active material, a positive electrode which contains either a lithium, the multiple oxides of transition metals and carbon materials or such mixture as a positive active material, and aforementioned nonaqueous electrolyte for rechargeable batteries.

[0041] Such a nonaqueous electrolyte rechargeable battery is applicable to for example, a cylindrical nonaqueous electrolyte rechargeable battery. It comes to contain a cylindrical nonaqueous electrolyte rechargeable battery with the cell can 5, where an electric insulating plate 4 is laid in the upper and lower sides of winding and a winding object through the SEPARE evening 3 into which the nonaqueous electrolyte for rechargeable batteries was poured for the negative electrode 1 which applies a negative-electrode active material to the negative-electrode charge collector 9, and becomes it as shown in drawing 1, and the positive electrode 2 which comes to apply a positive active material to the positive-electrode charge collector 10. the cell can 5 — the cell lid 7 — the ** ROGASU blanket 6 — minding — by closing, it is attached and connects with a negative electrode 1 or a positive electrode 2 electrically through negative-electrode lead 1 1 and positive-electrode lead 1 2, respectively, and it is constituted so that it may function as the negative electrode or positive electrode of a cell In addition, separator is a porous film.

[0042] By this cell, as for the positive-electrode lead 12, electrical installation with the cell lid 7 may be measured through the sheet metal 8 for current interception. By such cell, if the pressure inside a cell rises, the sheet metal 8 for current interception is pushed up, and deforms, positive-electrode lead 1 2 leave the above-mentioned sheet metal 8 and the welded portion, they are cut, and current has become as [intercept / current].

[0043] Although any of the carbon material as a negative-electrode active material which constitutes such a negative electrode 1 which can dope and ** dope a metal lithium, a lithium alloy, and a lithium ion can be used, it is desirable to use the carbon material which can dope and ** dope a lithium ion among these. Such a carbon material may be an amorphous carbon even if it is graphite, and all carbon materials, such as activated carbon, a carbon fiber, carbon black, and a meso carbon micro bead, are used.

[0044] Especially in this invention, the spacing (d002) of the field (002) measured with X-ray analysis is 0.37nm or less, and if the carbon material which has a property near the graphite whose density is three or more 1.70 g/cm is desirable and uses such a carbon material, the energy density of a cell can be made high. Moreover, the multiple oxide which the multiple oxide which consists of the lithium and transition metals of transition-metals oxides, such as MoS2, TiS2, MnO2, and V2O5, and a transition-metals sulfide or LiCoO2 and LiMnO2, LiMn 2O4, and LiNiO2 grade is used as a positive active material which constitutes a positive electrode 2, and especially consists of a lithium and transition metals is desirable.

[0045] Moreover, when a negative electrode is a lithium metal or a lithium alloy, a carbon material can also be used as a positive electrode. The mixture of a lithium, the multiple oxide of transition metals, and a carbon material can also be used as a positive electrode further again. Moreover, the nonaqueous electrolyte rechargeable battery concerning this invention is applicable also to a coin type nonaqueous electrolyte rechargeable battery as shown in drawing 2.

[0046] the coin type nonaqueous electrolyte rechargeable battery of drawing 2 — the shape of a disk — the shape of negative-electrode 1 3 and a disk — positive-electrode 1 4, separator 15, and stainless board 1 7 — a negative electrode 13, separator 1 5, and a positive electrode 1 — 4 and where a laminating is carried out in the stainless sequence of board 1 7, it contains to cell can 1 6 — having — the cell can (lid) 19 — gasket 1 8 — minding — it is attached by closing The same thing as the above is used as negative-electrode 1 3, separator 1 5, and positive-electrode 1 4. Moreover, the thing of the quality of the material of the stainless steel which cannot corrode cell can 1 6 and cell can (lid) 1 9 easily due to the electrolytic solution is used.

[0047] In addition, it may not be limited to what showed the configuration of a cell etc. to drawing 1 and drawing 2 including the nonaqueous electrolyte for rechargeable batteries which explained the nonaqueous electrolyte rechargeable battery concerning this invention above as the electrolytic solution, but you may be a square shape etc.

[0048]

[Effect of the Invention] The nonaqueous electrolyte for rechargeable batteries concerning this invention is fire retardancy, and excellent in charge/discharge capability ability, and the nonaqueous electrolyte rechargeable battery using such nonaqueous electrolyte for rechargeable batteries is safe, can generate the high voltage, and is excellent in a charge-and-discharge property.

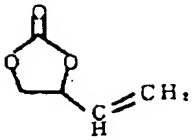
[0049]

[Example] Although an example is given and this invention is explained concretely hereafter, this invention is not limited at all by these examples.

[0050] Vinyl ethylene carbonate in the nonaqueous electrolyte for rechargeable batteries after dissolving example 1 <manufacture of nonaqueous electrolyte for rechargeable batteries> LiPF615.2g (100mmol) in trimethyl phosphate (TMPA) (VEC)

[0051]

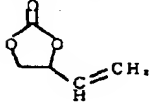
[Formula 18]



It added so that concentration might become 5% of the weight, and the nonaqueous electrolyte for rechargeable batteries was prepared (electrolyte concentration of 1.0 mols/l.).
<production of a negative electrode> — the negative electrode 13 was produced as follows first
[0052] 95 weight sections and the polyvinylidene-fluoride (PVDF) 5 weight section of a binder are mixed in the carbon-powder end of the mesophase pitch micro fiber Made from PETOKA (tradename : MEMBUROMMIRUDO, d 002= 0.336nm, density 2.21 g/cm3), and it distributes to N-methyl pyrrolidone of a solvent — making — a negative electrode — a mixture — the slurry (the shape of a paste) was prepared this negative electrode — a mixture — after making the negative-electrode charge collector with a thickness of 20 micrometers made from band-like copper foil apply and dry a slurry, the band-like carbon negative electrode was obtained such a negative electrode — the thickness of a mixture was 25 micrometers Furthermore, after piercing this band electrode with a diameter of 15mm in the shape of a disk, it pressed and considered as the negative-electrode electrode 13.
The <production of positive electrode> positive electrode 14 was produced as follows.
[0053] the LiCoO2 (21 8 micrometers of mean particle diameters [Product name : HLC-]) particle 91 weight section by Honjo Chemical, the graphite 6 weight section of electric conduction material, and the polyvinylidene-fluoride 3 weight section of a binder — mixing — a positive electrode — preparing a mixture and distributing N-methyl pyrrolidone — a positive electrode — a mixture — the slurry was obtained The positive-electrode charge collector made from a band-like aluminum foil with a thickness of 20 micrometers was made to apply and dry this slurry, it pressed, and the band-like positive electrode was obtained. such a positive electrode — the thickness of a mixture was 40 micrometers It considered as the positive-electrode electrode 14 by furthermore piercing this band electrode with a diameter of 15mm in the shape of a disk.
<production of a cell> — as shown in drawing 2 , after carrying out the laminating of the disk-like negative electrode 13 obtained by doing in this way, the disk-like positive electrode 14, and the separator 15 (micrometers [in thickness / 25], fine porosity polypropylene film with a diameter of 19mm) to the cell can 16 of 2032 sizes made from stainless steel in the sequence of a negative electrode 13, separator 15, and a positive electrode 14, the aforementioned nonaqueous electrolyte for rechargeable batteries was poured into separator 15 Then, after containing the board 17 (the thickness of 2.4mm, diameter of 15.4mm) made from stainless steel, through the gasket 18 made from polypropylene, by closing the cell can (lid) 19, the airtightness in a cell was held and the coin type nonaqueous electrolyte rechargeable battery with a diameter [of 20mm] and a height of 3.2mm was produced.
<measurement of service capacity> — the service capacity of the nonaqueous electrolyte rechargeable battery which carried out in this way and was produced was measured In addition, in this example, the direction of current where Li+ is doped by the negative electrode was considered as charge, and the direction of current by which a ** dope is carried out was considered as electric discharge. Charge was performed by the 4.2V or 1mA constant-current constant-potential charge method, and when the charging current became below 50microA, it considered as the end. Electric discharge was performed by the 1mA constant current, and when voltage amounted to 2.7V, it considered as the end. From the charge capacity of this charge-and-discharge cycle, and service capacity, charge-and-discharge efficiency was calculated by the following formula. A result is shown in Table 1.
[0054]
[Equation 1]

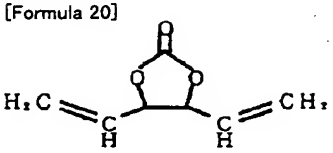
$$\text{充放電効率（%）} = \frac{\text{放電容量(mAh/g)}}{\text{充電容量(mAh/g)}} \times 100$$

[0055] The Manila paper for separators with a thickness of 0.04mm cut with a length of 30cm a 1 5mm and in the shape of a strip of paper in the beaker containing the nonaqueous electrolyte for the <self-extinguishing evaluation of nonaqueous electrolyte for rechargeable batteries> aforementioned rechargeable batteries was dipped 1 minute or more. The superfluous nonaqueous electrolyte for rechargeable batteries which drips from Manila paper was wiped with the beaker wall, the support needle of the sample base which has a support needle at intervals of 2.5cm was stabbed with Manila paper, and it fixed horizontally. The sample base which fixed Manila paper was put into the metal box of 25 cmx2 5 cmx5 0 cm, the end was lit with the writer, the length with which separator paper burned was measured, and the case where combustion length was under lcm was estimated that there is self-extinguishing. A result is shown in Table 1.
[0056] Vinyl ethylene carbonate in the nonaqueous electrolyte for rechargeable batteries after dissolving LiPF615.2g (100mmol) in the mixed solvent (mixed weight ratio EC:DMC:TMPA= 37.6:56.7:5.2) of ethylene carbonate (EC), dimethyl carbonate (DMC), and trimethyl phosphate (TMPA) like example 2 example 1 (VEC)
[0057]
[Formula 19]

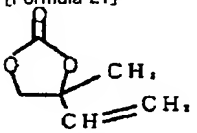


It added so that concentration might become 0.5% of the weight, and the charge-and-discharge efficiency of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 1 except having prepared the nonaqueous electrolyte for rechargeable batteries (electrolyte concentration of 1.0 mols/l.). A result is shown in Table 1.

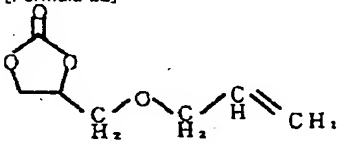
[0058] It sets in the example 3 example 2, and is 4 and 5-divinyl ethylene carbonate [0059] instead of vinyl ethylene carbonate.
[Formula 20]



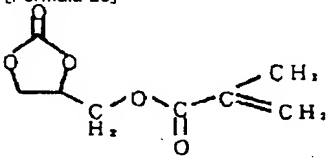
The charge-and-discharge efficiency of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 2 except having ******(ed). A result is shown in Table 1.
[0060] It sets in the example 4 example 2, and they are 4-methyl and 4-vinyl ethylene carbonate [0061] instead of vinyl ethylene carbonate.
[Formula 21]



The charge-and-discharge efficiency of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 2 except having ******(ed). A result is shown in Table 1.
[0062] It sets in the example 5 example 2, and is allyloxy methyl-ethylene carbonate [0063] instead of vinyl ethylene carbonate.
[Formula 22]



except for having ******(ed) — an example 2 — the same — carrying out — the charge-and-discharge efficiency of a cell — ** — self-extinguishing evaluation of the electrolytic solution — it carried out A result is shown in Table 1.
[0064] It sets in the example 6 example 2, and is metacryloxy methyl-ethylene carbonate [0065] instead of vinyl ethylene carbonate.
[Formula 23]



The charge-and-discharge efficiency of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 2 except having ******(ed). A result is shown in Table 1.
[0066]
[Table 1]

	非水溶媒組成(重量%)					初回充放電効率(%)	自己消火性
	EC	DMC	TMPA	環状カーボネート	添加量(重量%)		
実施例1	0	0	95.0	ビニルEC	5.0	87.3	あり
実施例2	37.6	56.7	5.2	ビニルEC	0.5	95.6	あり
実施例3	37.6	56.7	5.2	ジビニルEC	0.5	95.6	あり
実施例4	37.6	56.7	5.2	4-メチル,4-ビニルEC	0.5	89.8	あり
実施例5	37.6	56.7	5.2	アリルオキシメチルEC	0.5	89.4	あり
実施例6	37.6	56.7	5.2	メタクリルオキシメチルEC	0.5	90.5	あり

[Translation done.]

TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte rechargeable battery containing this electrolytic solution while relating to the nonaqueous electrolyte for rechargeable batteries which it is still more detailed, and fire retardancy is high, was safe, and could generate the high voltage, and was excellent in the cell charge-and-discharge property about the nonaqueous electrolyte for rechargeable batteries, and a nonaqueous electrolyte rechargeable battery.

[0002]

Background of the Invention] Nonaqueous electrolyte is used as the electrolytic solution of energy-storage devices, such as a lithium cell, and since these devices have a high voltage and high-energy density and are excellent in reliability, they are widely used for the power supply of consumer electronics etc. Nonaqueous electrolyte consists of a non-aqueous solvent and an electrolyte, and propylene carbonate [which is generally the organic solvent of a high dielectric constant], gamma-butyrolactone, sulfolane or dimethyl carbonate [that is the organic solvent of hypoviscosity], dimethoxyethane, tetrahydrofuran, 1, and 3-dioxolane etc. is used as a non-aqueous solvent. Moreover, as an electrolyte, Et4NBF4, LiBF4, LiPF6, LiClO4 and LiAsF6, LiCF3SO3, LiAlCl4, LiSiF6, etc. are used.

[0003] By the way, since a cell with a high energy density is desired, research is advanced about the high-voltage cell. For example, the rechargeable battery called rocking-chair type which used the lithium of LiCoO2, LiNiO2, and LiMn2O4 grade and the multiple oxide of transition metals for the positive electrode of a cell, and used the carbon material for the negative electrode is studied. since [in this case,] a cell voltage can generate more than 4V and moreover does not have a deposit of a metal lithium — overcharge and external short-circuit — ****(ing) — crushing — etc. — also by experiment, it is checked that safety is secured and it appears on the market as a noncommercial use However, when the future large formation of high-energy density and enlargement are made, to raise safety further is desired and it is called for that inflammable nonaqueous electrolyte has self-extinguishing. For this reason, adding the phosphoric ester known as a compound with self-extinguishing to the electrolytic solution is proposed (for example, refer to JP,4-184870,A).

[0004] However, although the electrolytic solution which added general phosphoric ester, such as phosphoric-acid triethyl, is fire retardancy and safety improved, depending on the kind and addition of phosphoric ester, there were also cell charge-and-discharge efficiency, an energy density of a cell, and a thing that cannot necessarily be satisfied in respect of a battery life. Although limiting the addition of phosphoric ester (for example, referring to JP,7-114940,A) etc. was proposed in order to solve such a problem for example, it was not what is not necessarily satisfied in respect of fire retardancy, safety, cell charge-and-discharge efficiency, the energy density of a cell, a battery life, etc.

[0005]

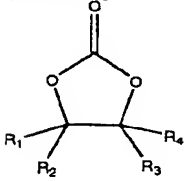
[Objects of the Invention] this invention aims at offering the rechargeable battery containing this nonaqueous electrolyte while it aims at offering the nonaqueous electrolyte for rechargeable batteries which was made in view of the above-mentioned trouble, fire retardancy was highly safe, and could generate the high voltage, and was excellent in cell charge/discharge capability ability.

[0006]

[Summary of the Invention] The nonaqueous electrolyte for rechargeable batteries concerning this invention is characterized by the bird clapper from the non-aqueous solvent containing the annular carbonate expressed with the following general formula [I], and a phosphoric ester compound, and the electrolyte.

[0007]

[Formula 5]



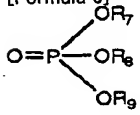
[I]

Among the formula [I], even if R1-R4 are mutually the same, you may differ. The carbon atomic number in which a hydrogen atom and a carbon atomic number include the alkyl group of 1-7 and a disconjugation system unsaturated bond The hydrocarbon group of 2-7, - It is CH2OR5 or -CH2OCOR6, and at least one of R1-R4 is a basis including a disconjugation system unsaturated bond.

[0008] That in which the carbon atomic number which includes a disconjugation system unsaturated bond in at least one of the annular carbonate expressed with the above-mentioned general formula [I], and R1-R4 has the hydrocarbon group of 2-7 is desirable, and it is desirable that it is an alkenyl machine especially. moreover, among the cyclic ester expressed with the above-mentioned general formula [I], and among R1-R4] — at least one -CH2OR5 or -CH2OCOR6 — it is (the carbon atomic number in which, as for R5 and R6, a carbon atomic number includes the alkyl group or disconjugation system unsaturated bond of 1-7 shows the hydrocarbon group of 2-7) — what it has is desirable

[0009] It is desirable that it is phosphoric ester expressed with following general formula [II] - [IV], and the aforementioned phosphoric ester compound is [0010].

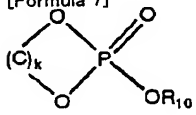
[Formula 6]



[II]

[0011]

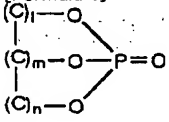
[Formula 7]



[III]

[0012]

[Formula 8]



[IV]

(Among a formula, even if R7-R10 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers. It is desirable especially that it is trimethyl phosphate. The thing of an annular carbonate and a chain-like carbonate for which the aforementioned non-aqueous solvent includes 1. kind at least is still more desirable. As for an electrolyte, it is desirable that it is lithium salt.

[0013] The nonaqueous electrolyte rechargeable battery concerning this invention is characterized by the negative electrode which contains a metal lithium, a lithium content alloy, or the carbon material in which the dope and ** doping of a lithium ion are possible as a negative-electrode active material, the positive electrode which contains either a lithium, the multiple oxides of transition metals and carbon materials or such mixture as a positive active material, and including the aforementioned nonaqueous electrolyte for rechargeable batteries as the electrolytic solution.

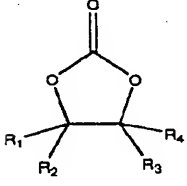
[0014]

[Detailed Description of the Invention] Hereafter, the nonaqueous electrolyte concerning this invention and the nonaqueous electrolyte rechargeable battery using this nonaqueous electrolyte are explained concretely. The nonaqueous electrolyte for rechargeable batteries concerning this invention consists of a non-aqueous solvent containing a specific annular carbonate and a specific phosphoric ester compound, and an electrolyte.

[0015] What is expressed with the following general formula [I] as an annular carbonate used by the annular carbonate this invention is used.

[0016]

[Formula 9]

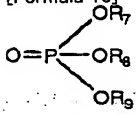


[I]

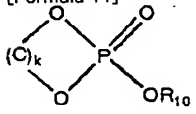
Among the formula [I], even if R1-R4 are mutually the same, you may differ. The carbon atomic number in which a hydrogen atom and a carbon atomic number include the alkyl group of 1-7 and a disconjugation system unsaturated bond The hydrocarbon group of 2-7, - It is CH2OR5 or -CH2OCOR6 (the carbon atomic number in which, as for R5 and R6, a carbon atomic number includes the alkyl group or disconjugation system unsaturated bond of 1-7 shows the hydrocarbon group of 2-7), and is the basis in which at least one of R1-R4 includes a disconjugation system unsaturated bond.

[0017] What the carbon atomic number in which at least one of R1-R4 includes a disconjugation system unsaturated bond has the hydrocarbon group of 2-7, and has -CH2OR5 or -CH2OCOR6 (the carbon atomic number in which R5 and R6 include a disconjugation system unsaturated bond shows the hydrocarbon group of 2-7) is desirable as cyclic ester expressed with such an above-mentioned general formula [I] by this invention. It is desirable that a carbon atomic number including such a disconjugation system unsaturated bond is an alkenyl machine as a hydrocarbon group of 2-7.

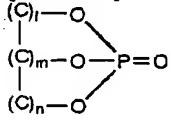
[0018] As an annular carbonate expressed with such a formula [I] 4-vinyl ethylene carbonate, 4, and 4-divinyl ethylene carbonate, Vinyl ethylene carbonate derivative;4-vinyl-4-methyl-ethylene carbonate, such as 4 and 5-divinyl ethylene carbonate, 4-vinyl-5-methyl-ethylene carbonate, the 4-vinyl -4, 5-dimethyl ethylene carbonate, The 4-vinyl -5, 5-dimethyl ethylene carbonate, 4-vinyl - Alkylation vinyl ethylene carbonate derivative;4-allyloxy methyl-ethylene carbonate, such as 4, 5, and 5-trimethylethylene carbonate, Allyloxy methyl-ethylene carbonate derivative;4-methyl-4-allyloxy methyl-ethylene carbonate, such as 4 and 5-diaryl oxymethyl ethylene carbonate, Alkylation allyloxy methyl-ethylene carbonate, such as 4-methyl-5-allyloxy methyl-ethylene carbonate; 4-acrylic oxymethyl ethylene carbonate, Acrylic oxymethyl ethylene carbonate derivative;4-methyl-4-acrylic oxymethyl ethylene carbonate, such as 4 and 5-JIAKURIRU oxymethyl ethylene carbonate, Alkylation acrylic oxymethyl ethylene carbonate, such as 4-methyl-5-acrylic oxymethyl ethylene carbonate, etc. is mentioned.
[0019] Among these, the thing containing vinyl ethylene carbonate derivatives, such as 4-vinyl ethylene carbonate, 4, and 4-divinyl ethylene carbonate, 4, and 5-divinyl ethylene carbonate, is desirable.
[0020] There is an effect of improving the charge-and-discharge efficiency of the cell produced in case a phosphoric ester compound is added, and the fall of a load characteristic in such an annular carbonate.
As a phosphoric ester compound used by the phosphoric ester compound this invention, the phosphoric ester expressed with following general formula [II] - [IV] is used preferably.
[0021]
[Formula 10]



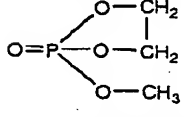
[II]
[0022]
[Formula 11]



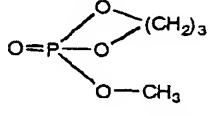
[III]
[0023]
[Formula 12]



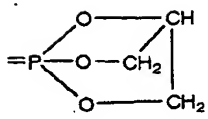
[IV]
(Among a formula, even if R7-R10 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers.
Specifically as phosphoric ester expressed with a formula [II], trimethyl phosphate, triethyl phosphate, TORIPURO pill phosphate, tributyl phosphate, dimethyl ethyl phosphate, methyl diethyl phosphate, etc. are mentioned. Specifically as phosphoric ester expressed with a formula [III], it is methyl-ethylene phosphate and [0024].
[Formula 13]



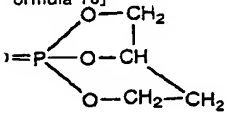
Methyl trimethylene phosphate [0025]
[Formula 14]



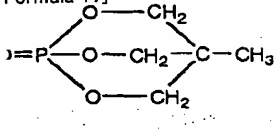
**** is mentioned. Specifically as phosphoric ester expressed with a formula [IV], it is [0026].
[Formula 15]



]027]
Formula 16]



0028]
Formula 17]



rimethylolethane phosphate etc. is mentioned.
0029] In respect of fire-resistant grant, since the effect is large, trimethyl phosphate and phosphoric-acid triethyl are iesirable, and especially trimethyl phosphate is [among these] desirable.
0030] In the nonaqueous electrolyte for rechargeable batteries concerning a non-aqueous-solvent this invention, the ion-aqueous solvent containing the annular carbonate expressed with the above general formulas [I] and a hosphoric ester compound is used. As for the aforementioned phosphoric-acid ESUDERU compound, in the binary ystem of an annular carbonate and a phosphoric ester compound, it is desirable to be preferably contained in 90 - 9.9% of the weight of the amount still more preferably 80 to 99.99% of the weight 60 to 99.999% of the weight in a ion-aqueous solvent. If the phosphoric ester compound is contained in the non-aqueous solvent in such an amount, ufficient fire retardancy for the nonaqueous electrolyte for rechargeable batteries can be given.
0031] Moreover, as for the annular carbonate expressed with a general formula [I], it is desirable to be preferably dded in 0.1 - 10% of the weight of the amount still more preferably 0.01 to 20% of the weight 0.001 to 40% of the veight to a non-aqueous solvent. The charge-and-discharge efficiency of the cell produced in case a phosphoric ester compound will be added, if the annular carbonate expressed with a general formula [I] in a non-aqueous solvent n such an amount is added, and the fall of a load characteristic are fully improvable.
[0032] With the non-aqueous solvent used by this invention In addition to the annular carbonate expressed with a general formula [I], and a phosphoric ester compound, it is desirable to contain carbonates, such as other annular carbonates and a chain-like carbonate. By including such a carbonate, the charge-and-discharge efficiency and the load characteristic of a cell are further improvable. As other annular carbonates, ethylene carbonate, propylene car PONETO, butylene carbonate, etc. are mentioned. these — one sort — or two or more sorts may use it, mixing The mixed solvent of ethylene carbonate, propylene carbonate or ethylene carbonate, and propylene carbonate is preferably used among these annular carbonates. If these annular carbonates are contained, it is possible to raise the solubility of the electrolyte in low temperature, transportation of an electrolyte can become easy, and the electrical conductivity of the electrolytic solution can be raised further.
[0033] As a chain-like carbonate, dimethyl carbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, ethyl propyl carbonate, etc. are mentioned. these — one sort — or two or more sorts may use it, mixing Since dimethyl carbonate can raise the self-extinguishing of the electrolytic solution among these chain-like carbonates, it is desirable.
[0034] If these chain-like carbonic acid ESUDERU is contained in the non-aqueous solvent, it is possible to make low viscosity of the nonaqueous electrolyte for rechargeable batteries, and electrolytic solubility can be raised further and it can consider as the electrolytic solution excellent in the electrical conductivity in ordinary temperature or low temperature. The above chain-like carbonates and annular carbonates can also be mixed and used.
[0035] In the case of the three-component system which mixes and uses other the above cyclic ester and chain-like carbonates for the annular carbonate and phosphoric ester compound which are expressed with a general formula [I], the annular carbonate expressed with a general formula [I] is 0.001 - 40 % of the weight usually preferably used at 0.1 - 5% of the weight of a rate still more preferably 0.01 to 20% of the weight to the non-aqueous-solvent whole quantity.

[0036] case [moreover,] it is the same — a phosphoric ester compound — the non-aqueous-solvent whole quantity — receiving — usually — 0.1 - 99.999 % of the weight — desirable — 1 - 99.99 % of the weight — further — desirable — 3 - 60 % of the weight — it comes out comparatively and is used — having — other cyclic ester and chain-like carbonates — the non-aqueous-solvent whole quantity — receiving — usually — 99.899 or less % of the weight — desirable — 98.9 or less % of the weight — further — desirable — 35 - 96.9 % of the weight — it comes out comparatively and is used
[0037] If it is possible to raise the electrical conductivity of the nonaqueous electrolyte for rechargeable batteries if other annular carbonates are contained in the non-aqueous solvent in such an amount and the chain-like carbonate is contained, the nonaqueous electrolyte for rechargeable batteries excellent in self-extinguishing can be obtained.
[0038] The annular carbonate expressed with the above-mentioned phosphoric ester and a general formula [I] to the non-aqueous solvent used by this invention further again, The methyl formate usually used as a non-aqueous solvent for cells besides other annular carbonates and a chain-like carbonate, An ethyl formate, a propyl formate, methyl acetate, ethyl acetate, propyl acetate, Chain-like ether, such as chain-like ester, such as a methyl propionate and an ethyl propionate, and dimethoxyethane, Amides, such as cyclic ether, such as a tetrahydrofuran, and a

hylformamide Methyl - ******-BAMETO, such as N and N-dimethyl carver mate Annular sulfones, such as c ester, such as gamma-butyrolactone, and a sulfolane Non-aqueous solvents, such as annular ureas, such as c-amides [, such as annular carver mates, such as N-methyl OKISASORIJINON and N-methyl pyrrolidone,], N, N-dimethyl imidazolidone, can be used to about 40 % of the weight to the whole quantity of a non-aqueous ent.

9] As an electrolyte used by the electrolyte this invention, usually, if used as an electrolyte for nonaqueous rolyte, it can be used, without being limited especially. Specifically LiPF6, LiBF4, LiClO4, LiAsF6, LiOSO2R11, LiN two R12) (SO two R13), R11-R18 among LiC (SO two R14) (SO two R15) (SO two R16) and a LiN(SO2OR17) OR18) [formula It may differ, even if mutually the same, and lithium salt, such as] and LiSiF6 which are the uoroalkyl machine of carbon numbers 1-6, LiC4F9SO3, and LiC3F17SO3, is used preferably. These lithium salt be used independently, and may mix and use two or more sorts of lithium salt.

0] Since LiPF6 and LiBF4 become [fire retardancy] high by the synergism with phosphoric ester among these m salt, it is desirable. As for such an electrolyte, it is usually desirable to contain 0.1-3 mols /in the nonaqueous rolyte for rechargeable batteries by the concentration of 0.5-2 mols/l. preferably l.

nonaqueous electrolyte rechargeable battery concerning a nonaqueous electrolyte rechargeable battery this ntion consists of a negative electrode which contains a metal lithium, a lithium content alloy, or the carbon rial in which the dope and ** doping of a lithium ion are possible as a negative-electrode active material, a ive electrode which contains either a lithium, the multiple oxides of transition metals and carbon materials or mixture as a positive active material, and aforementioned nonaqueous electrolyte for rechargeable batteries.

1] Such a nonaqueous electrolyte rechargeable battery is applicable to for example, a cylindrical nonaqueous trolyte rechargeable battery. It comes to contain a cylindrical nonaqueous electrolyte rechargeable battery with cell can 5, where an electric insulating plate 4 is laid in the upper and lower sides of winding and a winding object ugh the SEPARE evening 3 into which the nonaqueous electrolyte for rechargeable batteries was poured for the tive electrode 1 which applies a negative-electrode active material to the negative-electrode charge collector 9, becomes it as shown in drawing 1, and the positive electrode 2 which comes to apply a positive active material to positive-electrode charge collector 10, the cell can 5 — the cell lid 7 — the ** ROGASU blanket 6 — minding — losing, it is attached and connects with a negative electrode 1 or a positive electrode 2 electrically through tive-electrode lead 1 1 and positive-electrode lead 1 2, respectively, and it is constituted so that it may function he negative electrode or positive electrode of a cell In addition, separator is a porous film.

2] By this cell, as for the positive-electrode lead 12, electrical installation with the cell lid 7 may be measured ugh the sheet metal 8 for current interception. By such cell, if the pressure inside a cell rises, the sheet metal 8 current interception is pushed up, and deforms, positive-electrode lead 1 2 leave the above-mentioned sheet al 8 and the welded portion, they are cut, and current has become as [intercept / current].

3] Although any of the carbon material as a negative-electrode active material which constitutes such a negative trode 1 which can dope and ** dope a metal lithium, a lithium alloy, and a lithium ion can be used, it is desirable to the carbon material which can dope and ** dope a lithium ion among these. Such a carbon material may be an rphous carbon even if it is graphite, and all carbon materials, such as activated carbon, a carbon fiber, carbon k, and a meso carbon micro bead, are used.

4] Especially in this invention, the spacing (d002) of the field (002) measured with X-ray analysis is 0.37nm or , and if the carbon material which has a property near the graphite whose density is three or more 1.70 g/cm is irable and uses such a carbon material, the energy density of a cell can be made high. Moreover, the multiple oxide ch the multiple oxide which consists of the lithium and transition metals of transition-metals oxides, such as MoS2, 2, MnO2, and V2O5, and a transition-metals sulfide or LiCoO2 and LiMnO2, LiMn 2O4, and LiNiO2 grade is used as ositive active material which constitutes a positive electrode 2, and especially consists of a lithium and transition tals is desirable.

5] Moreover, when a negative electrode is a lithium metal or a lithium alloy, a carbon material can also be used as ositive electrode. The mixture of a lithium, the multiple oxide of transition metals, and a carbon material can also be d as a positive electrode further again. Moreover, the nonaqueous electrolyte rechargeable battery concerning this ntion is applicable also to a coin type nonaqueous electrolyte rechargeable battery as shown in drawing 2.

6] the coin type nonaqueous electrolyte rechargeable battery of drawing 2 — the shape of a disk — the shape of ative-electrode 1 3 and a disk — positive-electrode 1 4, separator 15, and stainless board 1 7 — a negative ctrode 13, separator 1 5, and a positive electrode 1 — 4 and where a laminating is carried out in the stainless uence of board 1 7, it contains to cell can 1 6 — having — the cell can (lid) 19 — gasket 1 8 — minding — it is ached by closing The same thing as the above is used as negative-electrode 1 3, separator 1 5, and itive-electrode 1 4. Moreover, the thing of the quality of the material of the stainless steel which cannot corrode l can 1 6 and cell can (lid) 1 9 easily due to the electrolytic solution is used.

7] In addition, it may not be limited to what showed the configuration of a cell etc. to drawing 1 and drawing 2 luding the nonaqueous electrolyte for rechargeable batteries which explained the nonaqueous electrolyte hargeable battery concerning this invention above as the electrolytic solution, but you may be a square shape etc.

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anslation done.]

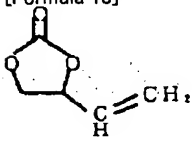
EFFECT OF THE INVENTION

[Effect of the Invention] The nonaqueous electrolyte for rechargeable batteries concerning this invention is fire retardancy, and excellent in charge/discharge capability ability, and the nonaqueous electrolyte rechargeable battery using such nonaqueous electrolyte for rechargeable batteries is safe, can generate the high voltage, and is excellent in a charge-and-discharge property.

[Translation done.]

EXAMPLE

[Example] Although an example is given and this invention is explained concretely hereafter, this invention is not limited at all by these examples.
[0050] Vinyl ethylene carbonate in the nonaqueous electrolyte for rechargeable batteries after dissolving example 1 <manufacture of nonaqueous electrolyte for rechargeable batteries> LiPF615.2g (100mmol) in trimethyl phosphate (TMPA) (VEC)
[0051]
[Formula 18]



It added so that concentration might become 5% of the weight, and the nonaqueous electrolyte for rechargeable batteries was prepared (electrolyte concentration of 1.0 mols/l.).
<production of a negative electrode> — the negative electrode 13 was produced as follows first
[0052] 95 weight sections and the polyvinylidene-fluoride (PVDF) 5 weight section of a binder are mixed in the carbon-powder end of the mesophase pitch micro fiber Made from PETOKA (tradename : MEMBUROMMIRUDO, d 002= 0.336nm, density 2.21 g/cm3), and it distributes to N-methyl pyrrolidone of a solvent — making — a negative electrode — a mixture — the slurry (the shape of a paste) was prepared this negative electrode — a mixture — after making the negative-electrode charge collector with a thickness of 20 micrometers made from band-like copper foil apply and dry a slurry, the band-like carbon negative electrode was obtained such a negative electrode — the thickness of a mixture was 25 micrometers Furthermore, after piercing this band electrode with a diameter of 15mm in the shape of a disk, it pressed and considered as the negative-electrode electrode 13.
The <production of positive electrode> positive electrode 14 was produced as follows.
[0053] the LiCoO2 (21 8 micrometers of mean particle diameters [Product name : HLC-]) particle 91 weight section by Honjo Chemical, the graphite 6 weight section of electric conduction material, and the polyvinylidene-fluoride 3 weight section of a binder — mixing — a positive electrode — preparing a mixture and distributing N-methyl pyrrolidone — a positive electrode — a mixture — the slurry was obtained The positive-electrode charge collector made from a band-like aluminum foil with a thickness of 20 micrometers was made to apply and dry this slurry, it pressed, and the band-like positive electrode was obtained. such a positive electrode — the thickness of a mixture was 40 micrometers It considered as the positive-electrode electrode 14 by furthermore piercing this band electrode with a diameter of 15mm in the shape of a disk.
<production of a cell> — as shown in drawing 2 , after carrying out the laminating of the disk-like negative electrode 13 obtained by doing in this way, the disk-like positive electrode 14, and the separator 15 (micrometers [in thickness / 25], fine porosity polypropylene film with a diameter of 19mm) to the cell can 16 of 2032 sizes made from stainless steel in the sequence of a negative electrode 13, separator 15, and a positive electrode 14, the aforementioned nonaqueous electrolyte for rechargeable batteries was poured into separator 15 Then, after containing the board 17 (the thickness of 2.4mm, diameter of 15.4mm) made from stainless steel, through the gasket 18 made from polypropylene, by closing the cell can (lid) 19, the airtightness in a cell was held and the coin type nonaqueous electrolyte rechargeable battery with a diameter [of 20mm] and a height of 3.2mm was produced.
<measurement of service capacity> — the service capacity of the nonaqueous electrolyte rechargeable battery which carried out in this way and was produced was measured In addition, in this example, the direction of current where Li+ is doped by the negative electrode was considered as charge, and the direction of current by which a ** dope is carried out was considered as electric discharge. Charge was performed by the 4.2V or 1mA constant-current constant-potential charge method, and when the charging current became below 50microA, it considered as the end. Electric discharge was performed by the 1mA constant current, and when voltage amounted to 2.7V, it considered as the end. From the charge capacity of this charge-and-discharge cycle, and service capacity, charge-and-discharge efficiency was calculated by the following formula. A result is shown in Table 1.
[0054]
[Equation 1]

$$\text{充放電効率（%）} = \frac{\text{放電容量(mAh/g)}}{\text{充電容量(mAh/g)}} \times 100$$

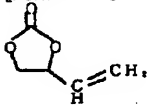
[0055] The Manila paper for separators with a thickness of 0.04mm cut with a length of 30cm a 1 5mm and in the shape of a strip of paper in the beaker containing the nonaqueous electrolyte for the <self-extinguishing evaluation of nonaqueous electrolyte for rechargeable batteries> aforementioned rechargeable batteries was dipped 1 minute or more. The superfluous nonaqueous electrolyte for rechargeable batteries which drips from Manila paper was wiped with the beaker wall, the support needle of the sample base which has a support needle at intervals of 2.5cm was

stabbed with Manila paper, and it fixed horizontally. The sample base which fixed Manila paper was put into the metal box of 25 cmx2 5 cmx5 0 cm, the end was lit with the writer, the length with which separator paper burned was measured, and the case where combustion length was under lcm was estimated that there is self-extinguishing. A result is shown in Table 1.

[0056] Vinyl ethylene carbonate in the nonaqueous electrolyte for rechargeable batteries after dissolving LiPF615.2g (100mmol) in the mixed solvent (mixed weight ratio EC:DMC:TMPA= 37.6:56.7:5.2) of ethylene carbonate (EC), dimethyl carbonate (DMC), and trimethyl phosphate (TMPA) like example 2 example 1 (VEC)

[0057]

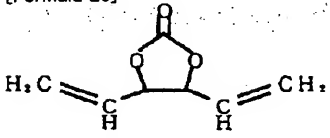
[Formula 19]



It added so that concentration might become 0.5% of the weight, and the charge-and-discharge efficiency of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 1 except having prepared the nonaqueous electrolyte for rechargeable batteries (electrolyte concentration of 1.0 mols/l.). A result is shown in Table 1.

[0058] It sets in the example 3 example 2, and is 4 and 5-divinyl ethylene carbonate [0059] instead of vinyl ethylene carbonate.

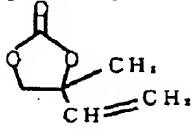
[Formula 20]



The charge-and-discharge efficiency of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 2 except having ******(ed). A result is shown in Table 1.

[0060] It sets in the example 4 example 2, and they are 4-methyl and 4-vinyl ethylene carbonate [0061] instead of vinyl ethylene carbonate.

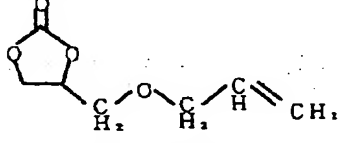
[Formula 21]



The charge-and-discharge efficiency of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 2 except having ******(ed). A result is shown in Table 1.

[0062] It sets in the example 5 example 2, and is allyloxy methyl-ethylene carbonate [0063] instead of vinyl ethylene carbonate.

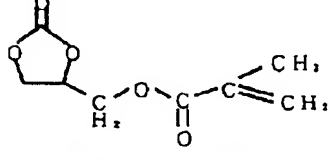
[Formula 22]



except for having ******(ed) — an example 2 — the same — carrying out — the charge-and-discharge efficiency of a cell — ** — self-extinguishing evaluation of the electrolytic solution — it carried out A result is shown in Table 1.

[0064] It sets in the example 6 example 2, and is metacryloxy methyl-ethylene carbonate [0065] instead of vinyl ethylene carbonate.

[Formula 23]



The charge-and-discharge efficiency of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 2 except having ******(ed). A result is shown in Table 1.

[0066]

[Table 1]

	非水溶媒組成(重量%)					初回充放電効率(%)	自己消火性
	EC	DMC	TMPA	環状カーボネート	添加量(重量%)		
実施例1	0	0	95.0	ビニルEC	5.0	87.3	あり
実施例2	37.6	56.7	5.2	ビニルEC	0.5	95.6	あり
実施例3	37.6	56.7	5.2	ジビニルEC	0.5	95.6	あり
実施例4	37.6	56.7	5.2	4-メチル,4-ビニルEC	0.5	89.8	あり
実施例5	37.6	56.7	5.2	アリルオキシメチルEC	0.5	89.4	あり
実施例6	37.6	56.7	5.2	メタクリルオキシメチルEC	0.5	90.5	あり

[Translation done.]

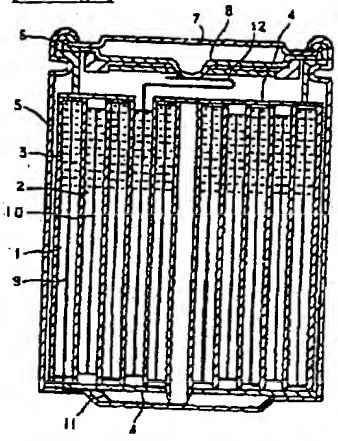
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the **** cross section of the cylindrical cell in which one example of the nonaqueous electrolyte rechargeable battery of this invention is shown.
[Drawing 2] It is the outline cross section of the coin cell in which one example of the nonaqueous electrolyte rechargeable battery of this invention is shown.
[Description of Notations]
1 13 .... Negative electrode
2 14 .... Positive electrode
3 15 .... Separator
4 11 .... Electric insulating plate
5 16 .... Cell can
6 .... Obturation gasket
7 .... Cell lid
8 .... Sheet metal for current interception
9 .... Negative-electrode charge collector
10 .... Positive-electrode charge collector
11 .... Negative-electrode lead
12 .... Positive-electrode lead
17 .... Board made from stainless steel
18 .... Gasket
19 .... Cell can (lid)

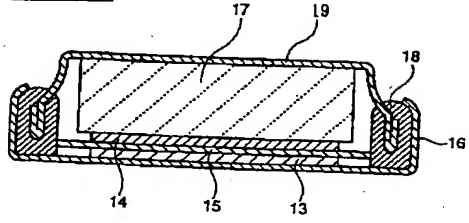
[Translation done.]

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]

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317/40		317/40	

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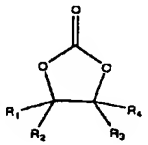
最終頁に続く

(54)【発明の名称】　二次電池用非水電解液及び非水電解液二次電池

(57)【要約】
【目的】難燃性であり充放電特性に優れた二次電池用非水電解液、及びこのような非水電解液を用いた、安全で高電圧を発生でき充放電特性に優れた非水電解液二次電池を得る。
【構成】下記一般式［Ｉ］で表される環状炭酸エステルとリン酸エステル化合物とを含む非水溶媒と、電解質からなることを特徴とする二次電池用非水電解液。
【化１】



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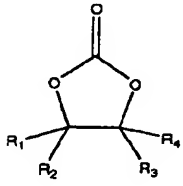
【特許請求の範囲】

【請求項１】　下記一般式［Ｉ］で表される環状炭酸エステルとリン酸エステル化合物とを含む非水溶媒と、電解質からなることを特徴とする二次電池用非水電解液。

【化１】



［Ｉ］

（式［Ｉ］中、R_1～R_4は互いに同一であっても異なっていてもよく、水素原子、炭素原子数が１～７のアルキル基、非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基、$-CH_2OR_5$、または$-CH_2OCOR_6$であり［R_5、R_6は炭素原子数が１～７のアルキル基、または非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基を示す］、かつR_1～R_4のうち、少なくとも一つが非共役系不飽和結合を含む基である。）

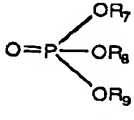
【請求項２】　上記一般式［Ｉ］で表される環状炭酸エステルが、R_1～R_4のうち少なくとも１つに非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基を有することを特徴とする、請求項１記載の二次電池用非水電解液。

【請求項３】　上記一般式［Ｉ］で表される環状炭酸エステルが、R_1～R_4のうち少なくとも１つに$-CH_2OR_5$、または$-CH_2OCOR_6$（R_5、R_6は非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基を示す。）を有するものであることを特徴とする、請求項１記載の二次電池用非水電解液。

【請求項４】　前記非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基が、アルケニル基であることを特徴とする、請求項１～３のいずれかに記載の二次電池用非水電解液。

【請求項５】　前記リン酸エステル化合物が下記一般式［II］～［IV］で表されるリン酸エステルであることを特徴とする請求項１に記載の二次電池用非水電解液。

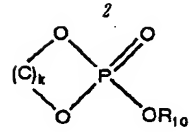
【化２】



［II］

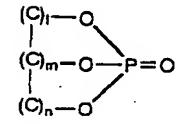
【化３】

2



［III］

【化４】



［IV］

（式中、R_7～R_{10}は互いに同一であっても異なっていてもよく、炭素数１～６のアルキル基またはフッ素置換アルキル基を示す。－(C)－は、直鎖状または分岐状の炭化水素基であり、k、l、m、nは炭素数を示し、kは２～８の整数であり、l、m、nは互いに同一であっても異なっていてもよく０～１２の整数であり、l、m、nの少なくともlつは１以上の整数である。）

【請求項６】　前記リン酸エステル化合物が、リン酸トリメチルであることを特徴とする請求項５記載の二次電池用非水電解液。

【請求項７】　前記非水溶媒が、前記［Ｉ］以外の環状炭酸エステル及び鎖状炭酸エステルから選ばれる少なくとも１種の炭酸エステルを更に含むことを特徴とする請求項１～６のいずれかに記載の二次電池用非水電解液。

【請求項８】　電解質がリチウム塩であることを特徴とする請求項１～７のいずれかに記載の二次電池用非水電解液。

【請求項９】　二次電池用非水電解液がリチウムイオン二次電池用電解液であることを特徴とする請求項１～８のいずれかに記載の二次電池用非水電解液。

【請求項１０】　負極活物質として金属リチウム、リチウム含有合金、リチウムイオンのドープ・脱ドープが可能な炭素材料のいずれかを含む負極と、正極活物質としてリチウムと遷移金属の複合酸化物、炭素材料またはこれらの混合物のいずれかを含む正極と、電解液として請求項１～９のいずれかに記載の二次電池用非水電解液とを有することを特徴とする非水電解液二次電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、二次電池用非水電解液および非水電解液二次電池に関し、更に詳しくは難燃性が高く安全で、高電圧を発生でき、かつ電池充放電特性の優れた二次電池用非水電解液に関するとともに、この電解液を含む非水電解液二次電池に関する。

【０００２】

【発明の技術的背景】非水電解液は、リチウム電池などエネルギー貯蔵デバイスの電解液として使用され、これ

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らのデバイスは高電圧・高エネルギー密度を有し、信頼性に優れているため、広く民生用電子機器の電源などに用いられている。非水電解液は、非水溶媒と電解質からなり、非水溶媒としては、一般に高誘電率の有機溶媒であるプロピレンカーボネート、γ－ブチロラクトン、スルホラン、あるいは低粘度の有機溶媒であるジメチルカーボネート、ジメトキシエタン、テトラヒドロフラン、1,3-ジオキソランなどが用いられている。また電解質としてはEt_4NBF_4、$LiBF_4$、$LiPF_6$、$LiClO_4$、$LiAsF_6$、$LiCF_3SO_3$、$LiAlCl_4$、$LiSiF_6$などが用いられている。

【0003】ところで、エネルギー密度の高い電池が望まれていることから、高電圧電池について研究が進められている。例えば,電池の正極に$LiCoO_2$、$LiNiO_2$、$LiMn_2O_4$等のリチウムと遷移金属の複合酸化物を使用し、負極に炭素材料を使用した、ロッキングチェア型と呼ばれる二次電池が研究されている。この場合、電池電圧は4V以上を発生することができ、しかも金属リチウムの析出がないため、過充電、外部ショート、釘刺し、押しつぶし等の実験によっても安全性が確保されることが確認され、民生用として出回るようになっている。しかしながら,今後の大幅な高エネルギー密度化、また、大型化がなされた場合には、さらに安全性を向上させることが望まれ、可燃性の非水電解液は自己消火性を有することが求められている。このため、自己消火性のある化合物として知られているリン酸エステル類を電解液に添加することが提案されている(たとえば特開平4-184870号公報参照)。

【0004】しかしながら,リン酸トリエチルなどの一般的なリン酸エステル類を添加した電解液は、難燃性であって安全性は向上されるが、リン酸エステルの種類や添加量によっては、電池充放電効率、電池のエネルギー密度、電池寿命の点で必ずしも満足できないものもあった。このような問題を解決するため,たとえば,リン酸エステルの添加量を限定すること(たとえば特開平7-114940号公報参照)などが提案されているが、難燃性、安全性、電池充放電効率、電池のエネルギー密度、電池寿命などの点で必ずしも満足するものではなかった。

【0005】

【発明の目的】本発明は、上記の問題点に鑑みなされたもので難燃性が高く安全で、高電圧を発生でき、かつ電池充放電性能の優れた二次電池用非水電解液を提供することを目的とするとともに、この非水電解液を含む二次電池を提供することを目的としている。

【0006】

【発明の概要】本発明に係る二次電池用非水電解液は,下記一般式［I］で表される環状炭酸エステルとリン酸エステル化合物とを含む非水溶媒と、電解質からなることを特徴としている。

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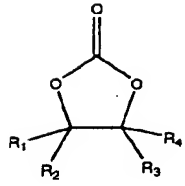
【0007】

【化5】



［I］

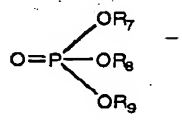
式［I］中、R_1～R_4は互いに同一であっても異なっていてもよく、水素原子、炭素原子数が1～7のアルキル基、非共役系不飽和結合を含む炭素原子数が2～7の炭化水素基、$-CH_2OR_5$、または$-CH_2OCOR_6$であり［R_5、R_6は炭素原子数が1～7のアルキル基、または非共役系不飽和結合を含む炭素原子数が2～7の炭化水素基を示す］、かつR_1～R_4のうち、少なくとも一つは非共役系不飽和結合を含む基である。

【0008】上記一般式［I］で表される環状炭酸エステルは、R_1～R_4のうち少なくとも1つに非共役系不飽和結合を含む炭素原子数が2～7の炭化水素基を有するものが好ましく、なかでもアルケニル基であることが好ましい。また、上記一般式［I］で表される環状エステルは、R_1～R_4のうち少なくとも1つに$-CH_2OR_5$、または$-CH_2OCOR_6$であり（R_5、R_6は炭素原子数が1～7のアルキル基、または非共役系不飽和結合を含む炭素原子数が2～7の炭化水素基を示す）を有するものが好ましい。

【0009】前記リン酸エステル化合物は、下記一般式［II］～［IV］で表されるリン酸エステルであることが好ましく,

【0010】

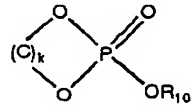
【化6】



［II］

【0011】

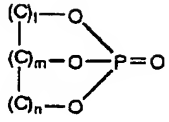
【化7】



［III］

【0012】

【化8】



[IV]

（式中、R_7～R_{10}は互いに同一であっても異なっていてもよく、炭素数１～６のアルキル基またはフッ素置換アルキル基を示す。－(C)－は、直鎖状または分岐状の炭化水素基であり、k、l、m、nは炭素数を示し、kは２～８の整数であり、l、m、nは互いに同一であっても異なっていてもよく０～１２の整数であり、l、m、nの少なくともlつは１以上の整数である。）特に、リン酸トリメチルであることが好ましい。前記非水溶媒は、さらに環状炭酸エステルと鎖状炭酸エステルの少なくともl.種を含むことが好ましい。電解質は、リチウム塩であることが好ましい。

【００１３】本発明に係る非水電解液二次電池は、負極活物質として金属リチウム、リチウム含有合金、リチウムイオンのドープ・脱ドープが可能な炭素材料のいずれかを含む負極と、正極活物質としてリチウムと遷移金属の複合酸化物、炭素材料またはこれらの混合物のいずれかを含む正極と、電解液として前記二次電池用非水電解液とを、含むことを特徴としている。

【００１４】

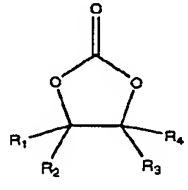
【発明の具体的説明】以下、本発明に係る非水電解液およびこの非水電解液を用いた非水電解液二次電池について具体的に説明する。本発明に係る二次電池用非水電解液は、特定の環状炭酸エステルとリン酸エステル化合物とを含む非水溶媒と、電解質とからなる。

【００１５】環状炭酸エステル

本発明で用いられる環状炭酸エステルとしては下記一般式［I］で表されるものが使用される。

【００１６】

【化９】



［I］

式［I］中、R_1～R_4は互いに同一であっても異なっていてもよく、水素原子、炭素原子数が１～７のアルキル基、非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基、$-CH_2OR_5$、または$-CH_2OCOR_6$であり（R_5、R_6は炭素原子数が１～７のアルキル基、または非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基を示す）、かつR_1～R_4のうち、少なくとも一つ

が非共役系不飽和結合を含む基である。

【００１７】本発明では、このような上記一般式［I］で表される環状エステルとして、R_1～R_4のうち少なくとも１つが、非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基を有するものであるか、あるいは$-CH_2OR_5$、または$-CH_2OCOR_6$（R_5、R_6は非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基を示す）を有するものが好ましい。このような非共役系不飽和結合を含む炭素原子数が２～７の炭化水素基としては、アルケニル基であることが好ましい。

【００１８】このような式［I］で表される環状炭酸エステルとしては、4-ビニルエチレンカーボネート、４，４－ジビニルエチレンカーボネート、４，５－ジビニルエチレンカーボネートなどのビニルエチレンカーボネート誘導体；４－ビニル－４－メチルエチレンカーボネート、４－ビニル－５－メチルエチレンカーボネート、４－ビニル－４，５－ジメチルエチレンカーボネート、４－ビニル－５，５－ジメチルエチレンカーボネート、４－ビニル－４，５，５－トリメチルエチレンカーボネートなどのアルキル置換ビニルエチレンカーボネート誘導体；４－アリルオキシメチルエチレンカーボネート、４，５－ジアリルオキシメチルエチレンカーボネートなどのアリルオキシメチルエチレンカーボネート誘導体；４－メチル－４－アリルオキシメチルエチレンカーボネート、４－メチル－５－アリルオキシメチルエチレンカーボネートなどのアルキル置換アリルオキシメチルエチレンカーボネート；４－アクリルオキシメチルエチレンカーボネート、４，５－ジアクリルオキシメチルエチレンカーボネートなどのアクリルオキシメチルエチレンカーボネート誘導体；４－メチル－４－アクリルオキシメチルエチレンカーボネート、４－メチル－５－アクリルオキシメチルエチレンカーボネートなどのアルキル置換アクリルオキシメチルエチレンカーボネートなどが挙げられる。

【００１９】このうち4-ビニルエチレンカーボネート、４，４－ジビニルエチレンカーボネート、４，５－ジビニルエチレンカーボネートなどのビニルエチレンカーボネート誘導体を含むものが好ましい。

【００２０】この様な環状炭酸エステルには、リン酸エステル化合物を添加する際に生じる電池の充放電効率および負荷特性の低下を改善する効果がある。

リン酸エステル化合物

本発明で用いられるリン酸エステル化合物として、下記一般式［II］～［IV］で表されるリン酸エステルが好ましく使用される。

【００２１】

【化１０】

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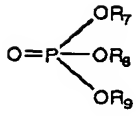
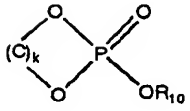


[II]

【００２２】

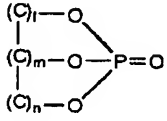
【化１１】



[III]

【００２３】

【化１２】



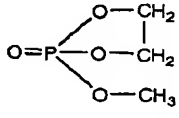
[IV]

（式中、R_7～R_{10}は互いに同一であっても異なっていてもよく、炭素数１～６のアルキル基またはフッ素置換アルキル基を示す。－(C)－は、直鎖状または分岐状の炭化水素基であり、ｋ、ｌ、ｍ、ｎは炭素数を示し、ｋは２～８の整数であり、ｌ、ｍ、ｎは互いに同一であっても異なっていてもよく０～１２の整数であり、ｌ、ｍ、ｎの少なくともｌつは１以上の整数である。）

式［II］で表されるリン酸エステルとして、具体的には、トリメチルホスフェート、トリエチルホスフェート、トリプロピルホスフェート、トリブチルホスフェート、ジメチルエチルホスフェート、メチルジエチルホスフェートなどが挙げられる。式［III］で表されるリン酸エステルとして、具体的には、メチルエチレンホスフェート、

【００２４】

【化１３】

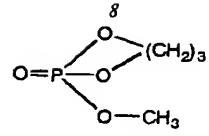


メチルトリメチレンホスフェート

【００２５】

【化１４】

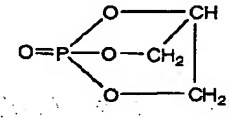
8



などが挙げられる。式［IV］で表されるリン酸エステルとして、具体的には、

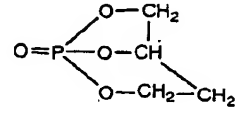
【００２６】

【化１５】



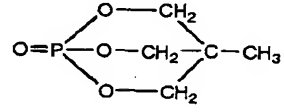
【００２７】

【化１６】



【００２８】

【化１７】



トリメチロールエタンホスフェートなどが挙げられる。

【００２９】これらのうち、リン酸トリメチル、リン酸トリエチルが難燃性付与の点で効果が大きいため好ましく、とくにリン酸トリメチルが好ましい。

【００３０】非水溶媒

本発明に係る二次電池用非水電解液では、上記のような一般式［Ｉ］で表される環状炭酸エステルとリン酸エステル化合物とを含む非水溶媒が使用される。環状炭酸エステルとリン酸エステル化合物との二成分系では、前記リン酸エステル化合物は、非水溶媒中に、６０～９９．９９９重量％、好ましくは８０～９９．９９重量％、さらに好ましくは９０～９９．９重量％の量で含まれていることが望ましい。このような量で非水溶媒中にリン酸エステル化合物が含まれていると、二次電池用非水電解液に十分な難燃性を付与することができる。

【００３１】また、一般式［Ｉ］で表される環状炭酸エステルは、非水溶媒に対して、０．００１～４０重量％、好ましくは０．０１～２０重量％、さらに好ましくは０．１～１０重量％の量で添加されていることが望ましい。このような量で非水溶媒中に一般式［Ｉ］で表される環状炭酸エステルが添加されていると，リン酸エステル化合物を添加する際に生じる電池の充放電効率およ

び負荷特性の低下を十分に改善することができる。

【００３２】本発明で用いられる非水溶媒では、一般式［Ｉ］で表される環状炭酸エステルとリン酸エステル化合物以外に、他の環状炭酸エステル、鎖状炭酸エステルなどの炭酸エステルが含まれていることが望ましい。このような炭酸エステルを含むことにより、さらに電池の充放電効率および負荷特性を改善することができる。他の環状炭酸エステルとしては,エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネートなどが挙げられる。これらは、１種または２種以上混合して使用してもよい。これらの環状炭酸エステルのうち、エチレンカーボネート、プロピレンカーボネートまたはエチレンカーボネートとプロピレンカーボネートとの混合溶媒が好ましく使用される。これらの環状炭酸エステルが含まれていると、低温における電解質の溶解度を高めることが可能であり、電解質の輸送が容易となり、さらに電解液の電気伝導度を向上させることができる。

【００３３】鎖状炭酸エステルとしては、ジメチルカーボネート、メチルエチルカーボネート、ジエチルカーボネート、メチルプロピルカーボネート、メチルイソプロピルカーボネート、エチルプロピルカーボネートなどが挙げられる。これらは、１種または２種以上混合して使用してもよい。これらの鎖状炭酸エステルのうち、ジメチルカーボネートが電解液の自己消火性を高めることができるので好ましい。

【００３４】これらの鎖状炭酸エスデルが非水溶媒中に含まれていると、二次電池用非水電解液の粘度を低くすることが可能であり、電解質の溶解度をさらに高めて、常温または低温での電気伝導性に優れた電解液とすることができる。以上のような鎖状炭酸エステルと環状炭酸エステルとは、混合して使用することもできる。

【００３５】一般式［Ｉ］で表される環状炭酸エステルとリン酸エステル化合物に、上記のような他の環状エステルや鎖状炭酸エステルを混合して使用する三成分系の場合には、一般式［Ｉ］で表される環状炭酸エステルは、非水溶媒全量に対し通常０．００１～４０重量%、好ましくは０．０１～２０重量%、更に好ましくは０．１～５重量%の割合で使用される。

【００３６】また同様の場合、リン酸エステル化合物は、非水溶媒全量に対し通常０．１～９９．９９９重量%、好ましくは１～９９．９９重量%、更に好ましくは３～６０重量%の割合で使用され、他の環状エステルや鎖状炭酸エステルは、非水溶媒全量に対し通常９９．８９９重量%以下、好ましくは９８．９重量%以下、更に好ましくは３５～９６．９重量%の割合で使用される。

【００３７】このような量で非水溶媒中に他の環状炭酸エステルが含まれていると、二次電池用非水電解液の電気伝導度を高めることが可能であり、また鎖状炭酸エステルが含まれていると、自己消火性に優れた二次電池用非水電解液を得ることができる。

【００３８】さらにまた本発明で用いる非水溶媒には、上記リン酸エステル、一般式［Ｉ］で表される環状炭酸エステル、他の環状炭酸エステル、鎖状炭酸エステルの他に、通常電池用非水溶媒として用いられる蟻酸メチル、蟻酸エチル、蟻酸プロピル、酢酸メチル、酢酸エチル、酢酸プロピル、プロピオン酸メチル、プロピオン酸エチルなどの鎖状エステル、ジメトキシエタンなどの鎖状エーテル類、テトラヒドロフランなどの環状エーテル類、ジメチルホルムアミドなどのアミド類、メチル-N,N-ジメチルカーバメートなどの鎖状カーバメート類、γ-ブチロラクトンなどの環状エステル類、スルホランなどの環状スルホン類、N-メチルオキサゾリジノンなどの環状カーバメート、N-メチルピロリドンなどの環状アミド、N,N-ジメチルイミダゾリドンなどの環状ウレア等の非水溶媒を、非水溶媒の全量に対し４０重量%程度迄使用することができる。

【００３９】電解質

本発明で使用される電解質としては、通常、非水電解液用電解質として使用されているものであれば、特に限定されることなく使用することができる。具体的には、$LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAsF_6$, $LiOSO_2R^{11}$, $LiN(SO_2R^{12})(SO_2R13)$, $LiC(SO_2R^{14})(SO_2R^{15})(SO_2R^{16})$, $LiN(SO_2OR^{17})(SO_2OR^{18})$［式中、$R^{11}$～$R^{18}$は、互いに同一であっても異なっていてもよく、炭素数１～６のパーフルオロアルキル基である］、$LiSiF_6$、$LiC_4F_9SO_3$、$LiC_3F_{17}SO_3$などのリチウム塩が好ましく使用される。これらのリチウム塩は単独で使用してもよく、また2種以上のリチウム塩を混合して使用してもよい。

【００４０】これらリチウム塩のうち、$LiPF_6$, $LiBF_4$がリン酸エステルとの相乗作用で難燃性が高くなるため好ましい。このような電解質は、通常、０．１～３モル/リットル、好ましくは０．５～２モル/リットルの濃度で二次電池用非水電解液中に含まれていることが望ましい。

非水電解液二次電池

本発明に係る非水電解液二次電池は、負極活物質として金属リチウム、リチウム含有合金、リチウムイオンのドープ･脱ドープが可能な炭素材料のいずれかを含む負極と、正極活物質としてリチウムと遷移金属の複合酸化物、炭素材料またはこれらの混合物のいずれかを含む正極と、前記の二次電池用非水電解液とから構成されている。

【００４１】このような非水電解液二次電池は、たとえば円筒型非水電解液二次電池に適用できる。円筒型非水電解液二次電池は、図1に示すように負極集電体9に負極活物質を塗布してなる負極1と、正極集電体10に正極活物質を塗布してなる正極2とを、二次電池用非水電解液を注入されたセパレータ3を介して巻回し、巻回体の上下に絶縁板4を載置した状態で電池缶5に収納してなるものである。電池缶5には電池蓋7が封口ガスケット6を介

してかしめることにより取り付けられ、それぞれ負極リード11および正極リード12を介して負極1あるいは正極2と電気的に接続され、電池の負極あるいは正極として機能するように構成されている。なおセパレータは多孔性の膜である。

【0042】この電池では、正極リード12は、電流遮断用薄板8を介して電池蓋7との電気的接続がはかられていてもよい。このような電池では、電池内部の圧力が上昇すると、電流遮断用薄板8が押し上げられ変形し、正極リード12が上記薄板8と溶接された部分を残して切断され、電流が遮断されるようなっている。

【0043】このような負極1を構成する負極活物質としては、金属リチウム、リチウム合金、リチウムイオンをドープ・脱ドープすることが可能な炭素材料のいずれを用いることができるが、これらのうちで、リチウムイオンをドープ・脱ドープすることが可能な炭素材料を用いることが好ましい。このような炭素材料は、グラファイトであっても非晶質炭素であってもよく、活性炭、炭素繊維、カーボンブラック、メソカーボンマイクロビーズ等あらゆる炭素材料が用いられる。

【0044】本発明では、特にX線解析で測定した(002)面の面間隔(d_{002})が0.37nm以下であり、密度が1.70g/cm3以上である黒鉛に近い性質を有する炭素材料が望ましく、このような炭素材料を使用すると、電池のエネルギー密度を高くすることができる。また正極2を構成する正極活物質としては、MoS_2、TiS_2、MnO_2、V_2O_5、などの遷移金属酸化物および遷移金属硫化物、または$LiCoO_2$、$LiMnO_2$、$LiMn_2O_4$、$LiNiO_2$等のリチウムと遷移金属とからなる複合酸化物を用いられ、特にリチウムと遷移金属とからなる複合酸化物が好ましい。

【0045】また、負極がリチウム金属またはリチウム合金である場合は、正極として炭素材料を用いることもできる。さらにまた、正極として、リチウムと遷移金属の複合酸化物と炭素材料との混合物を用いることもできる。また、本発明に係る非水電解液二次電池は、図2に示すようなコイン型非水電解液二次電池にも適用することができる。

【0046】図2のコイン型非水電解液二次電池では、円盤状負極13、円盤状正極14、セパレータ15およびステンレスの板17が、負極13、セパレータ15、正極14、ステンレスの板17の順序で積層された状態で電池缶16に収納され、電池缶(蓋)19がガスケット18を介してかしめることにより取り付けられている。負極13、セパレータ15、正極14としては、前記と同様のものが使用される。また電池缶16、電池缶(蓋)19は、電解液で腐食しにくいステンレスなどの材質のものが使用される。

【0047】なお、本発明に係る非水電解液二次電池は、電解液として以上説明した二次電池用非水電解液を含むものであり、電池の形状などは図1および図2に示したものに限定されず、角型などであってもよい。

【0048】

【発明の効果】本発明に係る二次電池用非水電解液は、難燃性であり充放電性能に優れ、このような二次電池用非水電解液を用いた非水電解液二次電池は、安全で、高電圧を発生でき、充放電特性に優れる。

【0049】

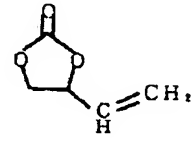
【実施例】以下、実施例を挙げて本発明を具体的に説明するが、本発明はこれら実施例により何ら限定されるものではない。

【0050】実施例1

<二次電池用非水電解液の調製>$LiPF_6$15.2g(100mmol)を、リン酸トリメチル(TMPA)に溶解したのち、二次電池用非水電解液中のビニルエチレンカーボネート(VEC)

【0051】

【化18】



濃度が5重量%になるように添加し、二次電池用非水電解液を調製した(電解質濃度1.0mol/リットル)。

<負極の作製>まず、負極13を以下のようにして作製した。

【0052】(株)ペトカ製のメソフェーズピッチマイクロファイバー(商品名:メンブロンミルド、d_{002}=0.336nm、密度2.21g/cm3)の炭素粉末95重量部と、結着剤のポリフッ化ビニリデン(PVDF)5重量部とを混合し、溶剤のN-メチルピロリドンに分散させ、負極合剤スラリー(ペースト状)を調製した。この負極合剤スラリーを厚さ20μmの帯状銅箔製の負極集電体に塗布し、乾燥させたのち、帯状の炭素負極を得た。このような負極合剤の厚さは25μmであった。さらに、この帯状電極を直径15mmの円盤状に打ち抜いた後、圧縮成形し負極電極13とした。

<正極の作製>正極14は以下のようにして作製した。

【0053】本庄ケミカル(株)製の$LiCoO_2$(製品名:HLC-21、平均粒径8μm)微粒子91重量部と、導電材のグラファイト6重量部と、結着剤のポリフッ化ビニリデン3重量部とを混合して正極合剤を調製し、N-メチルピロリドンに分散させることにより、正極合剤スラリーを得た。このスラリーを厚さ20μmの帯状アルミニウム箔製正極集電体に塗布し、乾燥させ、圧縮成形して、帯状正極を得た。このような正極合剤の厚さは40μmであった。さらにこの帯状電極を直径15mmの円盤状に打ち抜くことにより正極電極14とした。

<電池の作製>このようにして得られた円盤状負極13、

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円盤状正極14、およびセパレータ15（厚さ25μm、直径19mmの微多孔性ポリプロピレンフィルム）を図２に示すようにステンレス製の２０３２サイズの電池缶16に、負極１３、セパレータ１５、正極１４の順序で積層したのち、セパレータ１５に前記二次電池用非水電解液を注入した。その後、ステンレス製の板17（厚さ2.4mm、直径15.4mm）を収納した後、ポリプロピレン製のガスケット18を介して、電池缶（蓋）１９をかしめることにより、電池内の気密性を保持し、直径20mm、高さ3.2mmのコイン型非水電解液二次電池を作製した。

＜放電容量の測定＞このようにして作製した非水電解液二次電池の放電容量を測定した。なお、本実施例では、負極にLi^+がドープされる電流方向を充電、脱ドープされる電流方向を放電とした。充電は、4.2V、1mA定電流定電圧充電方法で行い、充電電流が５０μA以下になった時点で終了とした。放電は、１mAの定電流で行い、電圧が2.7Vに達した時点で終了とした。この充放電サイクルの充電容量と放電容量とから、次式により充放電効率を計算した。結果を表１に示す。

【００５４】

【数１】

$$\text{充放電効率（\%）} = \frac{\text{放電容量(mAh/g)}}{\text{充電容量(mAh/g)}} \times 100$$

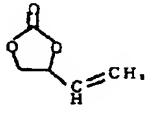
【００５５】＜二次電池用非水電解液の自己消火性評価＞前記二次電池用非水電解液の入ったビーカー中に、15mm、長さ30cmの短冊状に切断した厚さ0.04mmのセパレーター用マニラ紙を1分以上浸した。マニラ紙から滴り落ちる過剰の二次電池用非水電解液をビーカー壁で拭い、マニラ紙を2.5cm間隔で支持針を有するサンプル台の支持針に刺して水平に固定した。マニラ紙を固定したサンプル台を25 cm×2 5 cm×5 0 cmの金属製の箱に入れ，一端をライターで着火し、セパレーター紙の燃えた長さを測定し、燃焼長が1cm未満の場合を自己消火性があると評価した。結果を表1に示す。

【００５６】実施例２

実施例１と同様に、$LiPF_6$15.2g(100mmol)をエチレンカーボネート（ＥＣ）、ジメチルカーボネート（ＤＭＣ）とリン酸トリメチル（ＴＭＰＡ）との混合溶媒（混合重量比ＥＣ：ＤＭＣ：ＴＭＰＡ＝３７．６：５６．７：５．２）に溶解したのち、二次電池用非水電解液中のビニルエチレンカーボネート（ＶＥＣ）

【００５７】

【化１９】



濃度が0.5重量％になるように添加し、二次電池用非水

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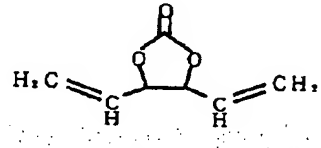
電解液を調製した（電解質濃度1.0mol／リットル）以外は実施例１と同様にして、電池の充放電効率と電解液の自己消火性を評価した。結果を表１に示す。

【００５８】実施例３

実施例２において、ビニルエチレンカーボネートの代わりに4,5-ジビニルエチレンカーボネート

【００５９】

【化２０】



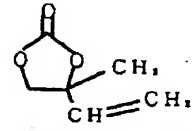
を使用した以外は実施例２と同様にして、電池の充放電効率と電解液の自己消火性を評価した。結果を表１に示す。

【００６０】実施例４

実施例２において、ビニルエチレンカーボネートの代わりに４－メチル，４－ビニルエチレンカーボネート

【００６１】

【化２１】



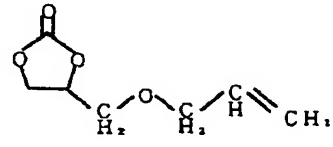
を使用した以外は、実施例２と同様にして、電池の充放電効率と電解液の自己消火性を評価した。結果を表１に示す。

【００６２】実施例５

実施例２において、ビニルエチレンカーボネートの代わりにアリルオキシメチルエチレンカーボネート

【００６３】

【化２２】



を使用した以外は実施例２と同様にして、電池の充放電効率をと電解液の自己消火性評価した。結果を表１に示す。

【００６４】実施例６

実施例２において、ビニルエチレンカーボネートの代わりにメタクリルオキシメチルエチレンカーボネート

【００６５】

【化２３】

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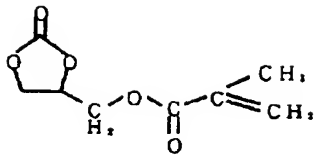

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を使用した以外は実施例２と同様にして、電池の充放電効率と電解液の自己消火性を評価した。結果を表１に示す。

【００６６】

【表１】

	非水溶媒組成(重量%)					初回充放電効率(%)	自己消火性
	EC	DMC	TMPA	環状カーボネート	添加量(重量%)		
実施例1	0	0	95.0	ビニルEC	5.0	87.3	あり
実施例2	37.6	56.7	5.2	ビニルEC	0.5	95.6	あり
実施例3	37.6	56.7	5.2	シスビニルEC	0.5	95.6	あり
実施例4	37.6	56.7	5.2	4-メチル,4-ビニルEC	0.5	89.8	あり
実施例5	37.6	56.7	5.2	アリルオキシメチルEC	0.5	89.4	あり
実施例6	37.6	56.7	5.2	メタクリルオキシメチルEC	0.5	90.5	あり

【図面の簡単な説明】

【図１】本発明の非水電解液二次電池の一実施例を示す円筒型電池の概略断面図である。

【図２】本発明の非水電解液二次電池の一実施例を示すコイン電池の概略断面図である。

【符号の説明】

1,13····負極

2,14····正極

3,15····セパレータ

4,11····絶縁板

5,16····電池缶

6····封口ガスケット

7····電池蓋

8····電流遮断用薄板

9····負極集電体

10····正極集電体

11····負極リード

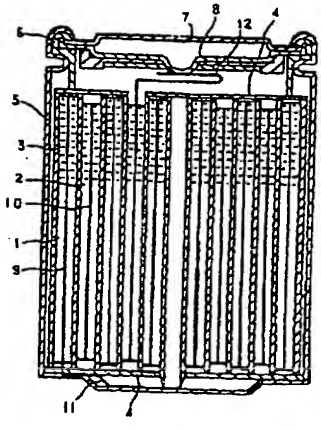
12····正極リード

17····ステンレス製の板

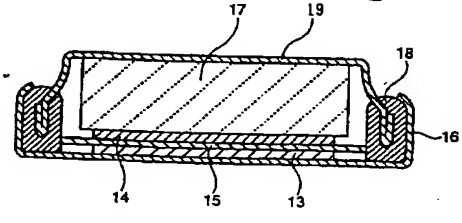
18····ガスケット

19····電池缶(蓋)

【図１】



【図２】



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